The role of NOM fouling for the retention of estradiol and ibuprofen during ultrafiltration

Jerman, D. ; Pronk, W. ; Boller, M. ; Schäfer, A.I. ; (2009) The role of NOM fouling on the retention of estradiol and ibuprofen during UF for drinking water production, Journal of Membrane Science, 329, 75-84.

The role of NOM fouling for the retention of estradiol and ibuprofen during ultrafiltration

Doris Jermann[a], *Wouter Pronk*[a], *Markus Boller*[a], *Andrea I. Schäfer*[b]

AUTHOR ADDRESS [a]Swiss Federal Institute of Aquatic Science and Technology (Eawag), 8600 Dübendorf, Switzerland

[b]School of Engineering and Electronics, The University of Edinburgh, UK

CORRESPONDING AUTHOR FOOTNOTE (doris.jermann@eawag.ch, phone: +41 44 823 50 92, fax: +41 44 823 53 89

ABSTRACT

The impact of membrane fouling by natural organic matter (NOM) on the behavior of micropollutants during ultrafiltration (UF) was investigated. Batch experiments with radioactively labeled estradiol and ibuprofen in the presence of NOM model compounds (alginate, Nordic aquatic and Aldrich humic acid) were performed using a hydrophilic and a hydrophobic membrane. The results indicate that the impact of the NOM fractions studied on micropollutant retention correlated with the fouling mechanism of the individual NOM fractions. NOM substances of high molecular weight such as alginate and Aldrich HA that foul the membrane by pore blocking and cake/gel formation had a greater impact than the Nordic aquatic humic acid of lower molecular weight. The effect of cake formation was attributed partly to micropollutant-NOM partitioning and subsequent NOM retention and partly to the effect of the fouling layer itself acting as a kind of second membrane. Fouling by NOM cake/gel formation led to a significantly increased retention of estradiol, whereas the impact of fouling on ibuprofen retention was negligible due to significantly lower Log K_{oc} values of ibuprofen compared to estradiol. Moreover, NOM adsorption on the membrane can lower the adsorption of hydrophobic micropollutants. Membrane adsorption of estradiol was in the order of mg/m^2 and was largely reversible with caustic solutions. The results of this study may prove useful for predicting the mass flow of micropollutants in UF applications.

KEYWORDS

Ultrafiltration, natural organic matter, fouling mechanisms, estradiol, ibuprofen

INTRODUCTION

Ultrafiltration (UF) is a well-established technology for the efficient and sustainable removal of pathogens and turbidity during drinking water production. Fouling is critical for UF processes, as it reduces process performance and impacts product quality (1, 2). Natural organic matter (NOM) is known as the major foulant during UF. Whereas early research suggested that humic substances were the main foulants, more recently polysaccharides have been found to cause detrimental fouling despite being present in small concentrations compared to humic substances (1-4). Although pore blocking and cake formation are the main fouling mechanisms for polysaccharides, these mechanisms apply to humic substances only to a limited extent because the latter also foul membranes by adsorption (1-4).

NOM is known to interact with various substances in the water, including micropollutants. As a consequence, NOM governs their transport and fate in the natural environment and during water-treatment processes. Micropollutants have acquired great attention during the last decade due to increased awareness of their hazardous nature in the aquatic environment (5, 6). This applies also to endocrine-disrupting compounds, because of their ecotoxicological effect, e.g. with regard to fish reproduction (7-9). Pharmaceuticals are also of serious public concern due to their potential negative effects on human and animal health, also considering the fact that many cases have been reported where the concentration in surface waters was in the same order or higher than the PNEC value (predicted no effect concentration) (10-13).

Considering the fact that the molecular weight cut-off of UF membranes (10-100 kDa) is at least one order of magnitude above the molecular weight of most micropollutants (< 1 kDa, see Table 1), the sieving effect can not result in substantial micropollutant removal. Although adsorption onto some UF membranes can lead to their retention in the initial filtration period, this is not considered to be a long-term removal mechanism (14-17). Furthermore, biological transformation of micropollutants can be relevant in systems with biological activity such as membrane bioreactors (18). However, biodegradation is negligible in systems with regular backwash with low concentrations of sanitizers applied in UF membrane plants used for drinking water production (19). In the case of NF and RO, the membrane sieving effect results in (partial) removal of most of organic micropollutants (16, 17, 20).

The presence of NOM during ultrafiltration can lead to competition for adsorption sites, resulting in lowered adsorption rates of micropollutants in NOM containing waters, as reported for the filtration of endocrine disrupting compounds in lake Ontario water (14). Furthermore, the presence of NOM can influence micropollutant rejection by partitioning of the micropollutant in suspended solids and partitioning in the fouling layer, as reported for the ultrafiltration of bisphenol A in greywater (21). Also the mechanisms of pore blocking and concentration polarization by NOM (humic acids) were reported to influence the retention of bisphenol A in nanofiltration processes (22).

Cake layer formation by NOM can also occur during ultrafiltration processes (1), and therefore it can be expected that also during ultrafiltration the presence of NOM can have an influence on the rejection of micropollutant. However, no systematic investigations have been published on this subject. In our study, we used two different micropollutants and three different NOM fractions (a polysaccharide and two humic acid types) in order to assess the mechanisms of this influence. Both compounds are relevant micropollutants, considering the endocrine disrupting effect of estradiol and the fact that ibuprofen (an anti-inflammatory drug) is found in relatively high concentrations in surface waters (23, 24). In order to avoid analytical inaccuracies associated with measuring micropollutants at environmentally relevant concentrations, radioactively labeled micropollutants were used in this study.

Jerman, D. ; Pronk, W. ; Boller, M. ; Schäfer, A.I. ; (2009) The role of NOM fouling on the retention of estradiol and ibuprofen during UF for drinking water production, Journal of Membrane Science, 329, 75-84.

MATERIAL AND METHODS

NOM foulants and solution chemistry

The selected NOM fractions were the polysaccharide alginate (alginic acid, Sigma Aldrich, UK, 12-80 kDa) and two different humic acids (HA), the IHSS Nordic Aquatic HA (International Humic Substances Society, US, 1-5 kDa) and the Aldrich HA (AHA, Sigma Aldrich, UK, 50 kDa). As outlined above polysaccharides and humic substances are major UF foulants. NOM stock solutions of 200 mg C/L were prepared without prefiltration to avoid loss of NOM fractions by adsorbing onto filters.

The concentrations used were 0-40 mg C/L for both HA, and 0-8 mg C/L of alginate. The NOM concentrations used are higher than in natural surface waters (eg. 1-5 mg DOC/L in Swiss lakes (25)) to enhance fouling. The solutions containing micropollutants and NOM were stirred overnight. Background solutions consisted of deionized water (DI), NaCl (20 mM) and $NaHCO_3$ (1 mM). The pH was adjusted to pH 7.5 with 0.2 M HCl/NaOH and the consistency of the ionic strength was checked by conductivity measurements. The pH and ionic strength were designed to represent conditions in Swiss lake waters, which are typically oligotrophic and of low conductivity and hardness (25).

Micropollutant model compounds

Estradiol and ibuprofen were selected for this study because these two substances of concern are found in the effluent of Swiss waste-water treatment plants and surface waters (6, 23, 24). A further selection criterion was that ibuprofen is negatively charged at neutral pH whereas estradiol is neutral at the same pH. The impact of the micropollutant charge could therefore be investigated. Intrinsic physiochemical properties of estradiol and ibuprofen and their molecular structures are given in Table 1.

Radioactively labeled estradiol ([2, 4, 6, 7-3H] – Estradiol, GE Health Care, USA) and ibuprofen (Ibuprofen, RS, [3H(G)], American Radiolabeled Chemicals, Inc, USA) were used as they allowed low concentrations to be detected. Stock solutions of radio-labeled (0.1 mg/L) micropollutants were prepared in pure methanol, stored below 4º C and used within one month. The concentration used in the experiments was 100 ng/L and comparable to the concentration ranges detected in Swiss lakes (24). In the case of the relatively hydrophobic membrane (see section *UF experiments*), estradiol was largely retained. In order to investigate the estradiol adsorption potential of the membrane, UF experiments with various higher concentrations up to 10 mg estradiol/L were performed (solubility of estradiol in DI 13 mg/L (16)). Due to the large estradiol sorption onto the hydrophobic membrane (see section *Retention of estradiol and ibuprofen without NOM*), 5 mg estradiol/L was used when estradiol was mixed with NOM fractions to allow a more sensitive analysis (concentrations used in all experiments are listed in Table S1 in Supporting Information). Labeled estradiol was supplemented with unlabeled estradiol (Sigma Aldrich, UK, stock solution was prepared in pure methanol) when concentrations above 100 ng estradiol/L were used.

Table 1 Physiochemical properties of estradiol (25) and ibuprofen (26) and their molecular structures.

UF experiments

Two different types of flat-sheet membranes – a polyethersulfone (PES, 100 kDa, Biomax, Millipore UK) and a regenerated cellulose membrane (RC, 100 kDa, Ultracel, Millipore UK) - were used to assess the impact of membrane hydrophobicity. PES membranes are more hydrophobic (contact angle 56° ± 3) than RC membranes (contact angle 26° ± 3) (27)[1]. A fresh membrane was used for every

[1] Information about hydrophobicity can be obtained by contact angle measurements with low hydrophobicities given by low contact angles.

experiment. Prior to use, the membranes were soaked overnight in DI water and then washed and preconditioned (0.5 bar) until a stable flux was observed.

The UF test unit was a batch filtration cell (400 mL, Amicon, membrane filtration area 42 cm^2) connected to a feed pump (gear pump) and a glass reservoir (5 L). The cell pressure and solution level in the cell were regulated via a pressure control device with limit values of 0.5 bar ± 0.01. No stirring conditions were applied. The permeate was collected in "Schott"-bottles on a balance connected to a PC that logged and recorded data every 30 seconds.

In order to assess the potential loss of micropollutants in the filtration device, a preliminary run through the system without a membrane was performed for each micropollutant. The loss of both micropollutants in the experimental device was found to be < 3 %.

Prior to every experiment, the clean membrane flux was assessed with DI. Before starting the experiment, the system was filled with the solution used in the experiments. A total of one liter was filtrated and the 100 mL permeate fractions were sampled separately. In the case of an overnight experiment (using 10 mg C/L alginate), a collective sample fraction from 500-900 mL was collected. The first 10 mL of permeate of every experimental run were discarded to avoid dilution of the permeate samples by residual DI in the membranes and system.

Moreover, separate experiments with previously HA-fouled hydrophobic (Biomax) membranes and estradiol were performed. Thus 1 L HA solution (without micropollutant) was filtered, the membrane was then rinsed with DI water and subsequently 1 L of micropollutant solution (without HA) was filtered. The permeate was sampled and analyzed as described in the following section.

In order to complete the mass balance of the micropollutants and investigate the cleaning efficiency of different chemical solutions, the membranes were subject to a standardized rinsing procedure. For this purpose, the membranes were first rinsed with DI and then cut into four pieces. Each piece was immersed in a separate bottle with 100 mL DI, hydrochloric acid (0.002 M), sodium hydroxide (0.002 M) or acetone and shaken for 45 minutes. Afterwards, 1 mL of each solution was analyzed in the scintillation counter as described below. The acetone was evaporated at room temperature prior to analysis because it was assumed to interfere with the scintillation liquid in the Scintillation Counter. It was previously ensured that 100 % (± 2.6 %) of the micropollutant remained in the vial while the acetone evaporated.

Analytical methods

The HA was quantified by UV spectrometry (Varian, CARY.100scan, Australia, 254 nm). A total organic carbon (TOC) analyzer (TOC-V, Shimadzu UK) was used to measure the alginate concentration. For the TOC analysis, experiments without micropollutants were performed in view of the high carbon content of the methanol used to make up the micropollutant stock solutions. The standard deviation of the standard solution (1 mg C/L) measurements was 5 %.

The micropollutants were analyzed by a scintillation counter (LS 6500 Multipurpose Scintillation Counter, Beckman Coulter TM USA, counting time 10 minutes, counting three times repeated (29)). The analyzed sample volume was 1 mL added to 7 mL of scintillation liquid (Ultima Gold LLT, PackardBioscience B.V., The Netherlands) (29). The detection limit was 4 ng/L.

Retention calculations

The observed retention (R) of the substances studied during UF filtration was calculated by Equation 1 (30).

$$R_n = 1 - \frac{C_{p(n)}}{C_f} \qquad \textbf{(1)}$$

C_p and C_f are the concentrations of the permeate and initial feed respectively, the subscript n giving the permeate fraction number. It should be noted that the observed retention is not equal to the

membrane retention, which is calculated by replacing the feed concentration in eq. (1) with the concentration at the membrane surface. The latter can be significantly higher than the feed concentration due to the concentration polarization of solutes at the membrane surface (30). However, the concentration at the membrane surface could not be measured with our experimental set up. The concentration in the cell could be measured at the end of an experiment and was used to complete the mass balance.

The retention during UF was calculated for the NOM (R_{NOM}) and the two micropollutants estradiol and ibuprofen (R_{mp}). The R_{mp} in the presence of NOM is the sum of the retention by the (virgin) membrane ($R_{mp\text{-}membrane}$) and the retention due to the presence of NOM. The latter was measured as the retention at the end of the experiments with micropollutants and NOM. The $R_{mp\text{-}membrane}$ results from the experiments without NOM. The presence of NOM can influence the retention of micropollutants due to NOM-partitioning of the micropollutants and an effect of the NOM fouling layer acting like a second membrane. Hence the retention due to the presence of NOM was calculated in this study as the sum of the retention due to NOM-partitioning ($R_{mp\text{-}NOM}$) and retention by the dynamic NOM-fouling layer ($R_{mp\text{-}fl}$) (see Equation (2)). It has to be noted that the $R_{mp\text{-}membrane}$ can also be affected by NOM in solution due to competition of NOM and micropollutants for membrane adsorption sites.

$$R_{mp} = R_{mp-membrane} + R_{mp-NOM} + R_{mp-fl} \qquad \textbf{(2)}$$

The value of $R_{mp\text{-}NOM}$ can be estimated from Log K_{OC}[2] (or Log K_{OM}[3] respectively). Log K_{OC} reference values for estradiol and the NOM compounds used are given in Table 2. They were chosen because they refer to two previous studies run under conditions (pH 7, 0.02 M NaCl) similar to those of our study. The label * refers to the study of Neale et al. (29) using the same estradiol and NOM concentrations in a similarly low range (12.5 mg C/L) to this study. The results of the study labeled with * were therefore used as a reference for our calculations. No reference values with the NOM fractions used were found for ibuprofen. However, the Log K_{oc} values of ibuprofen onto digested sludge (2.5 - min. 1.8, max. 3.1) are significantly lower than for estradiol (3.4 - min. 3.1, max. 3.7) (31). This indicates that the sorption of ibuprofen onto NOM is about ten times lower than that of estradiol onto NOM.

Table 2 Log K_{oc} values for estradiol with humic acids and alginate.

RESULTS

Retention of estradiol and ibuprofen without NOM

Figure 1 shows the retention of ibuprofen and estradiol by the two membranes without the presence of NOM. The flux decline during micropollutant filtration was insignificant. Experiments in triplicate showed deviations of ± 3.5 % in the retention values.

It can be seen in Figure 1 that the retention is relatively low (8 %) for estradiol and insignificant for ibuprofen with the hydrophilic membrane (RC). The retention of both micropollutants is significantly greater with the hydrophobic (Biomax) membrane. In the case of ibuprofen, the retention is initially higher (25 %) and then levels off to values of around 7 % with the filtrated volume showing classic breakthrough behavior (16). The estradiol retention is high throughout the filtration (80 %) with the hydrophobic membrane. These characteristics indicate adsorption of ibuprofen and estradiol - both compounds are hydrophobic to some extent - onto the hydrophobic membrane (16, 17, 20). Other retention mechanisms such as size exclusion are unlikely due to the large pore size of the UF membrane compared to the MW of the compounds. The significantly larger membrane adsorption of estradiol (85 % declining to 77 %) compared to ibuprofen (25 % declining to 7 %) can be explained by

[2], [3] K_{OC} and K_{OM} are used to relate the concentration of a certain micropollutant sorbed (partitioned) onto organic carbon and onto organic matter respectively to the freely dissolved concentration of the same micropollutant.

the higher K_{oc} value of estradiol, which indicates a greater affinity of estradiol to the membrane than ibuprofen (20, 31) (see section *Retention calculations*). Estradiol is uncharged and ibuprofen is negatively charged at pH 7.5 (Table 1). The negative charge of ibuprofen at pH 7.5 increases the charge repulsion between ibuprofen and the membrane because the membrane is also negatively charged at pH 7.5 (33). It has recently been shown that the membrane adsorption of ibuprofen is lower for negatively charged than for uncharged ibuprofen (20). This reduced affinity is an expression of the effective hydrophobicity of ibuprofen towards membranes at a given pH.

The capacity of the membrane for estradiol adsorption was further investigated as shown in Figure 1b. Breakthrough of the estradiol during filtration of 1 L volume was only observed above 1 mg estradiol/L. Further experiments with estradiol in the presence of NOM with the hydrophobic membrane were performed with 5 mg estradiol/L. The results are discussed below.

Figure 1 UF of estradiol and ibuprofen: a) Retention by hydrophobic (Biomax) and hydrophilic (RC) membrane, b) Retention of estradiol by hydrophobic (Biomax) membrane for solutions with different estradiol concentrations.

Our results for the retention of micropollutants, particularly estradiol, due to membrane adsorption by hydrophobic interactions, are in line with other studies reporting adsorption of hydrophobic micropollutants onto hydrophobic UF and NF membranes (14-17, 20, 34). However, the estradiol adsorption capacity of the hydrophobic membrane (758-780 mg/m^2 membrane) used is relatively high compared to the values reported in other studies with a polysulfone and a composite NF membrane (3.2 µg and 5 µg/m^2 respectively) (16, 34). This can be partly explained by the fact that these studies measured the adsorption during cross-flow filtration and static adsorption (no flow) and not during batch filtration as in our study. It had already been observed that the adsorption of estrone was lower in static adsorption than in dynamic filtration experiments (34). This was explained by the limited penetration of estrone and significant adsorption only at the membrane surface (35). However, the high adsorption of estradiol onto the PES membrane indicates a great affinity of estradiol for PES. Apart from the membrane material, the membrane structure can further impact the adsorption capacity (34). The large estradiol adsorption capacity observed for the Biomax membrane can be explained by noting that according to the manufacturers' data sheet it is a high-flux ultrafiltration membrane of high porosity associated with a high pore surface area, which results in numerous adsorption sites.

In this study, the recovery of estradiol was investigated by soaking the hydrophobic membranes used for the UF of estradiol (solutions with 2, 3 and 5 mg estradiol/L) in acid and caustic solutions, and in acetone. The results are shown in Figure 2, where 100 % refers to the estradiol that was retained on the membrane according to the mass balance. It can be seen that over 90 % of the estradiol retained on the membrane could be recovered with acetone, allowing the mass balance to be completed. The missing percentage is attributed to experimental and analytical errors (see section *Analytical methods)*.

Moreover, Figure 2 shows that the recovery of estradiol from the membrane increased with a rising concentration of sodium hydroxide. A solution with 0.02 M sodium hydroxide (pH 12.3) - used in many practical applications to clean membranes - dissolved up to 80 % of the estradiol. The strong effect of sodium hydroxide can be explained by the fact that estradiol is negatively charged above its pKa (10.4), which weakens its adhesion onto the negatively charged membrane (36). However, compound adsorption onto the membrane is often considered as a short-term effect relevant at the initial stage of filtration (14-17). Nevertheless, these results show that high-pH compounds may be released during membrane cleaning procedures, thus leading to partial recovery of the initial adsorption capacity (37).

Figure 2 Estradiol recovered from the membrane by deionized water (DI), HCl, NaOH and acetone after filtration of solutions with 2, 3 and 5 mg estradiol/L. 100% refers to the estradiol retained on the membrane on the basis of an estradiol UF mass balance of 1 L solution. Experiments performed in duplicate are differentiated by a and b

NOM retention and flux decline

In this section, the NOM fouling mechanisms are first discussed by analyzing the flux decline and the retention of the NOM used before relating the NOM fouling mechanisms to the observed micropollutant retention in the following sections. Figure 3 shows the flux decline (a-c) and the retention characteristics (d-f) during UF of the various NOM compounds.

The flux decline caused by the three types of NOM compounds could be classified as alginate > Aldrich HA > IHSS HA. It has to be noted that HA led to less fouling than alginate, although higher concentrations were used. The retention values correlated with the flux decline and were the largest for alginate (> 0.5), followed by Aldrich HA (> 0.2) and IHSS HA (< 0.05).

The retention and fouling effect of Aldrich HA significantly exceeded that of IHSS HA. This can be explained by the greater MW (average 50 kDa) of Aldrich HA compared to IHSS HA (average 10 kDa) and the significant percentage (30 %) of Aldrich HA with a molecular weight higher than the membrane MWCO of 100 kDa (37). This indicates that Aldrich HA membrane fouling occurred to some extent in the form of pore blocking/cake formation, which was not relevant in the case of IHSS HA (33, 38).

Figure 3 Flux declines and NOM retention during UF of NOM with estradiol and ibuprofen using the hydrophilic (cellulose) and hydrophobic (Biomax) membrane a) and d) IHSS humic acid (IHSS HA) b) and e) Aldrich HA (AHA), c) and f) alginate (AA). In Figure 3a, the flux reductions for NOM solution with estradiol (E) or ibuprofen (I) are given separately due to significant differences not observed in Figures 3b and 3c.

Moreover, it can be seen that the retention of IHSS and Aldrich HA initially declines, in particular with the hydrophobic (Biomax) membrane. This indicates initial adsorption of both HA types used onto the hydrophobic membrane (3, 33, 37). The IHSS HA membrane adsorption is discussed in more detail in one of our previous publications (32).

Alginate filtration resulted in a detrimental flux decline, thus confirming earlier findings on its strong fouling tendency (33, 38). Alginate filtration was characterized by an initially strong flux decline, and a weaker constant decline in a later filtration stage. The alginate retention increased with filtration time. These observations indicate fouling by initial pore blockage and additional cake/gel formation in a later stage (33, 38).

Finally, the retention and flux decline of alginate and Aldrich HA is similar with both membranes despite their different properties. This indicates the formation of a cake/gel that acts like a second membrane and governs the flux decline. The fact that the MW of Aldrich HA (3-300 kDa, (37)) and alginate (12-80 kDa) are in the range of the membrane pore size (100 kDa) makes it likely for size exclusion and cake formation to occur (32, 37).

Considering all the flux and retention data, it can be concluded that the dominating fouling mechanism for Aldrich HA and alginate is cake/gel formation. Initial pore blocking was observed with alginate, whereas membrane adsorption was initially relevant with Aldrich HA. In contrast, the only significant fouling mechanism in the case of IHSS HA was initial HA membrane adsorption.

Retention of estradiol and ibuprofen with Aldrich HA

Figure 4 shows the retention of estradiol and ibuprofen in the presence of Aldrich HA. In Figure 4a, it can be seen that the ibuprofen retention by the hydrophobic (Biomax) membrane decreases significantly in the presence of Aldrich HA, especially initially (25 % declined to 15 %). This can be explained by the membrane adsorption of humic acid lowering that of ibuprofen (14, 15, 20). This effect is discussed in detail later (section *Retention of estradiol/ibuprofen and HA membrane adsorption)*. After filtration of 200 mL, the retention differences in the presence and absence of Aldrich HA are no longer significant. This indicates that Aldrich HA has a negligible impact on the retention of ibuprofen apart from membrane adsorption. This finding was confirmed by the fact that Aldrich HA has an insignificant influence (3 %) on ibuprofen retention by the RC membrane (Figure 4c).

The results shown in Figures 4a and b show that the presence of Aldrich HA significantly increases the estradiol retention by both membranes (except in the initial phase with the Biomax membrane). This finding was further investigated by increasing the Aldrich HA concentration as shown in Figure 4b. It can be seen that the estradiol retention increases further when the Aldrich HA concentration is increased (5 % with 0 mg C/L, 13 % with 10 mg C/L and 25 % with 40 mg C/L). This effect correlates with increased Aldrich HA retention and fouling at the higher HA concentration (Figures 3b and 3e). This leads to the conclusion that estradiol retention increases significantly with enhanced fouling by Aldrich HA (as shown above), as further discussed below.

Figure 4 Estradiol and ibuprofen retention in the presence of Aldrich humic acid (mg C/L) a) estradiol and ibuprofen using the hydrophobic (Biomax) membrane, b) estradiol using the hydrophilic (RC) membrane at different concentrations of Aldrich HA, c) ibuprofen using the hydrophilic (RC) membrane.

Retention of estradiol and ibuprofen with alginate

Figure 5 shows the retention of estradiol and ibuprofen in the presence of alginate. In the case of ibuprofen, the presence of alginate led first to slightly increased and then to decreased ibuprofen retention by the hydrophobic (Biomax) and the hydrophilic (RC) membranes. Even negative ibuprofen retention values were observed towards the end of the UF. Such retention characteristics of the negatively charged ibuprofen can be explained by concentration polarization caused by the alginate fouling. The phenomenon of “cake-enhanced concentration polarization” has been previously reported in studies with reverse osmosis and nanofiltration membranes (20, 22, 39, 40). It implies that a fouling layer (or gel layer) can hinder the back-diffusion of smaller molecules and thereby increase the concentrations of small molecules, such as salts, at the membrane surface resulting in a higher concentration gradient of the small molecules across the membrane and thus a greater transport and a lower observed rejection of these molecules (22, 39). In order to verify that concentration polarization occurred in the experiments using alginate and ibuprofen, additional experiments were performed in which the solution in the filtration cell was stirred - to minimize concentration polarization - with the hydrophilic membrane. These experiments indeed showed a positive retention of ibuprofen in the presence of alginate (Figure S1 in Supporting Information). This confirms that concentration polarization was present in the alginate and ibuprofen experiments without stirring. It should however be noticed that the experiments without stirring are more representative for drinking water ultrafiltration processes, because in practice these processes are usually carried out in *dead-end* mode (without cross-flow).

In Figure 5, it can be observed that in the case of estradiol the retention by both membranes, Biomax and RC, is significantly increased when alginate is present (except in the initial phase with the Biomax membrane). This observation is similar to that made for estradiol and Aldrich HA. The estradiol

retention was investigated as a function of alginate concentration (Figure 5b). It increases further when the latter is increased (5 % with 0 mg C/L, 14 % with 1 mg C/L, 24 % with 4 mg C/L and 39 % with 10 mg C/L) , similar to the results shown above for Aldrich HA. This effect correlates with increased alginate retention and fouling at higher organic concentrations (Figures 3c and 3f) and indicates that estradiol retention increases with enhanced fouling by organic cake/gel formation.

Concentration polarization can affect the retention of a micropollutant as shown above with ibuprofen and alginate (20). It may also have been present in the experiments with estradiol and alginate. If this was the case, the estradiol retention would initially be lower than observed and then become greater than observed towards the end of the UF. Our experiments focused on dead-end operated systems with no shear component as most units in Switzerland are operated in this mode. In practice, capillary UF membranes are often used in the drinking-water industry and for dead-end operation the flow in the module can be regarded as semi-cross flow. It can be assumed that such hydraulic effects lead to a lower concentration polarization than observed in our experiments without stirring (30) A low concentration polarization may occur, in particular at the dead-end of the capillary where the cross-flow becomes insignificant. In cross flow operated units, concentration polarization will be also lowered, but depending on the cross flow velocity not be inexistent (30). Therefore the data here can provide a basis to understand the transport of micropollutants during UF.

Figure 5 Estradiol and ibuprofen retention in the presence of alginate (mg C/L) a) estradiol and ibuprofen with the hydrophobic (Biomax) membrane, b) estradiol with the hydrophilic (RC) membrane at different concentrations of alginate, c) ibuprofen with the hydrophilic (RC) membrane.

The qualitatively similar impact of alginate and Aldrich HA on the retention of estradiol and ibuprofen respectively correlates with the similar fouling characteristics of these substances observed. This leads to the conclusion that the individual NOM fouling mechanism determines the effect of NOM on the retention of a specific micropollutant during UF. Moreover, the greater effect of alginate on the retention of ibuprofen and estradiol compared to Aldrich HA correlates with the greater fouling by alginate and indicates that the extent of fouling is critical.

Estradiol retention by NOM partitioning

There are two possible mechanisms to explain the effect of Aldrich HA and alginate cake formation on estradiol retention. First, the estradiol retention can be increased by the presence of the fouling layer that may act as a secondary membrane (15-17, 20, 21). The second possibility is partitioning of estradiol onto NOM in solution and subsequent retention of the NOM. Estradiol partitioning onto NOM has been investigated by Neale et al. (29) using Aldrich HA and alginate in concentration ranges as low as in our study (12.5 mg C/L) and under similar conditions with regard to pH (7.0), ionic strength (0.02 M NaCl) and estradiol concentration (100 ng/L) (29). The results of this study were used to calculate the amount of estradiol partitioned onto Aldrich HA and alginate respectively, and hence to calculate the amount of estradiol retained due to NOM partitioning ($m_{R,mp\text{-}NOM}$) as given in Equation 3 (41).

$$m_{R,mp-NOM} = \frac{10^{-6} * K_{OC} * c_{OC}}{(10^{-6} * K_{OC} * c_{OC}) + 1} * m_{mp} * R_{NOM} \qquad \textbf{(3)}$$

The m_{mp} refers to the mass of micropollutant used, c_{OC} refers to the carbon concentration, $m_{mp\text{-}NOM}$ to the mass of estradiol partitioned onto the specific NOM fraction and R_{NOM} to the retention of the NOM fraction. K_{OC} is defined as the organic carbon partitioning coefficient and the values used in this study are shown in Table 2 marked as *.

In the case of Aldrich HA, the estradiol partitioning was calculated to be 13.6 ng/10 mg C HA. The total retention of Aldrich HA in our experiments was 0.2. Multiplication of this value by the estradiol

partitioned onto HA results in 2.7 ng of estradiol partitioned onto the retained HA. A mass balance of the UF experiments using 0 and 10 mg DOC Aldrich HA yields an additional retention of 5.7 ng estradiol when Aldrich HA is present compared to when it is absent. This leads to the estimation that the estradiol retention due to Aldrich HA partitioning accounts for 47% of the totally observed retention increase. The rest of the increased retention has to be attributed to the impact of the dynamic Aldrich HA fouling layer on the membrane. The same calculation was performed for the experiments with 40 mg C/L of Aldrich HA. It showed that an additional retention of 25.5 % of estradiol in the presence of Aldrich HA compared to its absence was due to NOM partitioning. The rest of the additionally retained estradiol was then attributed to the dynamic fouling layer. This lower percentage of estradiol retention due to NOM partitioning in the case of the increased humic acid concentration can be explained by the greater fouling in that case. This indicates that the impact of the dynamic fouling layer acting as a second membrane increases in proportion to the degree of fouling. However, it has to be considered with regard to such calculations that the estimated effect of NOM partitioning depends strongly on the reference used for K_{oc}.

In the case of alginate, the estradiol partitioned onto 4 mg C alginate was 3.5 ng and the total alginate retention was 0.55. Multiplication of the two values yields 1.9 ng of estradiol retained during UF due to alginate partitioning. The estradiol partitioning onto alginate thus accounted for only 15 % of the additionally retained estradiol in the presence of alginate (13.1 ng). The rest was caused by the dynamic alginate fouling layer. However, the relatively large impact of the dynamic alginate fouling layer on estradiol retention correlates with the strong fouling by alginate (Figure 2). The large flux decline with alginate indicates that this substance forms a rather dense cake/gel on the membrane, which can act as an additional second membrane for the transport of estradiol.

The results for alginate and Aldrich HA coincide with previous studies attributing an increased retention of endocrine substances in the presence of NOM both for NOM partitioning and in the presence of a NOM fouling layer (15, 21).

The different impacts of fouling by alginate and Aldrich HA on estradiol and ibuprofen retention is based on the different chemical characteristics of these two micropollutants and their partitioning onto NOM (Tables 1 and 2). Log K_{oc} values indicate that NOM partitioning is ten times lower for ibuprofen than for estradiol (31). NOM partitioning can consequently have a significant impact on the retention of estradiol but a minor impact on the retention of ibuprofen.

Retention of estradiol and ibuprofen with IHSS humic acid

Adsorption was the only significant fouling mechanism present with an IHSS HA membrane. This allowed the impact of NOM adsorption on the membranes, principally hydrophobic membranes, in the absence of cake formation, to be studied as shown in Figure 6.

Figure 6b shows that the estradiol retention was similar both in the presence and absence of IHSS HA when the hydrophilic membrane was used. This correlates well with an almost negligible IHSS HA retention by the hydrophilic membrane (Figure 2a).

Figure 6a shows a slightly lower estradiol and ibuprofen retention by the hydrophobic membrane in the presence of 10 mg C/L IHSS HA. The difference was statistically relevant only in the initial phase of ibuprofen filtration and correlated with the initial membrane adsorption of IHSS HA. This indicates that membrane adsorption of HA can lower the retention (caused by adsorption) of ibuprofen and estradiol as already suggested above by the results with Aldrich HA (14, 15, 20). However, no statistically relevant differences could be observed between the retentions of estradiol at 0, 10 and 40 mg C/L IHSS HA.

Figure 6 a) Estradiol and ibuprofen retention in the presence of IHSS HA (mg C/L) by the hydrophobic (Biomax) membrane, b) estradiol retention in the presence of IHSS HA (mg C/L) by the

hydrophilic (RC) membrane, c) estradiol retention in the presence of IHSS HA by the hydrophobic (Biomax) membrane pre-fouled with IHSS and Aldrich HA (AHA).

Retention of estradiol after membrane pre-fouling with HA

Additional experiments were performed in order to further investigate the effect of HA membrane adsorption on estradiol retention. The hydrophobic membranes (Biomax) were pre-fouled with IHSS and Aldrich HA before filtration of estradiol (without HA). Relative fluxes after HA pre-fouling were 0.8 (J/J_0) for IHSS and Aldrich HA independently of the HA concentration used. No further flux decline occurred during the subsequent estradiol filtration (data not shown). The membranes were rinsed with DI after pre-fouling with HA so that the HA remaining on the pre-fouled membrane may be attributed to HA adsorbed onto the membrane.

Figure 6c shows that membrane pre-fouling by IHSS HA decreased the estradiol retention significantly, and to a greater extent than filtration of the premixed compounds (Figure 6a). In addition, it can be seen that the estradiol retention decreased significantly after pre-fouling with Aldrich HA, although it increased when estradiol and Aldrich HA were premixed (Figure 3a). The opposite effect of Aldrich HA in the pre-mixed experiment is explained by the dominating effect of Aldrich HA cake formation, which increases the estradiol retention as discussed above. The Aldrich HA cake was not present in the experiment with pre-fouling as the membrane was rinsed with DI before filtration of estradiol, leaving only the adsorbed Aldrich HA on the membrane. However, these experiments clearly indicate that HA membrane adsorption decreased the retention of estradiol by the hydrophobic membrane (15, 16, 20, 35, 36).

Retention of estradiol/ibuprofen and HA membrane adsorption

The decreased retention of ibuprofen and estradiol when the membrane was fouled with HA can be explained by humic acid occupying adsorption sites for the micropollutants on the membrane surface (15, 16, 20, 35, 36). The effect is lower for pre-mixed UF because humic acid and estradiol compete for membrane surface and adsorption sites, which is not the case when the membrane is pre-fouled with HA. Moreover, humic acid adsorbed on the membrane can modify the latter's surface characteristics and thus reduce micropollutant-membrane interactions (14, 20, 42). In an earlier study, we showed that HA adsorption onto the same membrane as used here (Biomax) increases the negative charge of the membrane (33). A higher negative charge makes the membrane less hydrophobic and increases the charge repulsion between the membrane and the estradiol (20). It is consequently likely that it reduces the adsorption of estradiol onto the membrane.

Finally, our results show a greater decrease in estradiol retention when the membrane was pre-fouled by Aldrich HA than by IHSS HA. This can be explained by the fact that more Aldrich HA adsorbed onto the membrane than IHSS HA. This greater membrane adsorption is based on the higher molecular weight of Aldrich HA than IHSS HA (37). The hydrophobicity of humic acids increases with increasing molecular weight, which in turn increases the adsorption of humic acid onto hydrophobic membranes (42, 43).

CONCLUSIONS

Membrane fouling by NOM can significantly impact the transport of micropollutants during UF processes due to various NOM-micropollutant interactions in solution and during the NOM fouling process as summarized in Table 3. The impact was found to correlate with the individual NOM fouling mechanisms.

It was found that NOM of higher molecular weight – such as polysaccharides and Aldrich HA - had a greater impact on micropollutant retention than lower-MW NOM such as aquatic IHSS HA. This was ascribed to dominant membrane fouling by cake/gel formation by the high-MW NOM.

In the case of estradiol, it was shown that cake/gel formation can lead to increased micropollutant retention (up to 40% difference in retention). This was partly attributed to the partitioning of estradiol onto NOM and subsequent NOM retention. This mechanism was found to be mainly relevant to relatively hydrophobic NOM, such as humic substances, and its extent may be estimated from the Log K_{OC} value of a micropollutant Moreover, a retention effect of the fouling layer itself (acting as a second membrane) was suggested, particularly for the pronounced fouling by alginate. Finally, cake-enhanced concentration polarization was observed in the case of ibuprofen during the strong fouling by polysaccharides.

Further NOM-membrane adsorption can modify the membrane surface and reduce the membrane adsorption of micropollutants. This mechanism is mainly relevant to hydrophobic micropollutants, hydrophobic NOM and hydrophobic membranes, as it is based on hydrophobic interactions.

It was found that hydrophobic UF membranes can have a large adsorption capacity - in the range of hundreds of milligrams per m^2 membrane - for hydrophobic micropollutants such as estradiol. Because a large part of the estradiol can be released from the membrane by caustic cleaning solutions, the membrane adsorption capacity can be partly restored. With regard to practical applications, therefore, this indicates that adsorption of micropollutants onto membranes must be considered throughout their operation and not only initially. The results of this study may prove useful for predicting micropollutant mass flows in UF processes and assessing process risks.

ACKNOWLEDGMENTS

The authors wish to thank Alan Simm (School of Engineering and Electronics, The University of Edinburgh, UK) and Daniel Steiner (Eawag, Kastanienbaum, Switzerland) for their support in the laboratory work. We also wish to acknowledge the WVZ (Wasserversorgung Zürich) and WABAG AG, Winterthur, for their support and successful collaboration within the scope of the WAVE-21 project.

REFERENCES

[1] H. Huang, N. Lee, T. Young, A. Gary, J.C. Lozier, J.G. Jacangelo, Natural organic matter fouling of low-pressure, hollow-fibre membranes: Effects of NOM source and hydrodynamic conditions, Water Res., 41 (2007) 3823-3832.

[2] C. Jarusutthirak, G. Amy, J-Ph. Croue, Fouling characteristics of wastewater effluent organic matter (Efom) isolates on NF and UF membranes, Desalination, 145 (2002) 247-255.

[3] M.M. Clark, P. Lucas, Diffusion and partitioning of humic acid in a porous ultrafiltration membrane, J. Membr. Sci., 142 (1998) 13-25.

[4] K. Kimura, Y. Hane, Y. Watanabe, G. Amy, N. Ohkuma, Irreversible membrane fouling during ultrafiltration of surface water, Water Res., 30 (2004) 3431-3441.

[5] R.P. Schwarzenbach, B.I. Escher, K. Fenner, T.B. Hofstetter, C.A. Johnson, U. von Gunten, B. Wehrli, The challenge of micropollutants, Science 313 (2006) 1072-1077.

[6] E.L.M. Vermeirssen, O, Korner, R. Schonenberger, M.J.F. Sutter, P. Burkhardt-Holm, Characterization of environmental estrogens in river water using a three pronged approach: Active and passive water sampling and the analysis of accumulated estrogens in the bile of caged fish, Environ. Sci. Technol., 39 (2005) 8191-8198.

[7] T. Colborn, F.S. vom Saal, A.M. Soto, Developmental effects of endocrine-disrupting chemicals in wildlife and humans, Environ. Impact Assessment Review, 14 (1994) 469-489.

[8] J.P. Sumpter, A.C. Johnson, Lessons from endocrine disruption and their application to other issues concerning trace organics in the aquatic environment, Environ. Sci. Technol., 39 (2005) 4321-4332.

[9] C.R. Tyler, S.R. Jobling, J. P. Sumpter, Endocrine disruption in wildlife: A critical review of the evidence, Crit. Rev. Toxicol., 28 (1998) 319-361.
[10] T. Heberer, Occurrence, fate and removal of pharmaceutical residue in the aquatic environment: A review of recent research data, Toxicol. Lett., 131 (2002) 5-17.
[11] O.A.H. Jones, N. Voulvoulis, J.N. Lester, Aquatic Environmental Assessment of the Top 25 English Prescription Pharmaceuticals, Water Res., 36 (2002) 5013-5022.
[12] U. Jux, R.M. Baginski, H.-G. Arnold, M. Kronke, P.N. Seng, Detection of pharmaceutical contaminations of river, pond, and tap water from Cologne (Germany) and surroundings, Int. J. Hygiene and Environmental Health, 205 (2002) 393-398.
[13] F. Stuer-Lauridsen, M. Birkved, L.P. Hansen, H.C. Holten Lutzhoft, B. Halling-Sorensen, Environmental risk assessment of human pharmaceuticals in Denmark after normal therapeutic use, Chemosphere, 40 (2000) 783-793.
[14] A.M. Comerton, R.C. Andrews, D.M. Bagley, P. Yang, Membrane adsorption of endocrine disrupting compounds and pharmaceutically active compounds, , J. Membr. Sci., 303 (2007) 267-277.
[15] X. Jin, J. Hu, S.L. Ong, Influence of dissolved organic matter on estrone removal by NF membranes and the role of their structures, Water Res., 41 (2007) 3077-3088.
[16] L.D. Nghiem, A.I. Schäfer, M. Elimelech, Removal of natural hormones by nanofiltration membranes: Measurement, modeling and mechanisms, Environ. Sci. Technol., 38 (2004) 1888-1896.
[17] Y. Yoon, P. Westerhoff, S.A. Snyder, E.C. Wert, Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products, J. Membr. Sci., 270 (2006) 88-100.
[18] A. Joss, E. Keller, A. C. Alder, A. Göbel, C. S. McArdell, T. Ternes, H. Siegrist, Removal and pharmaceuticals and fragrances in biological wastewater treatment, Water Res., 39 (2005) 3139-3152.
[19] J.-M. Laine, C. Campos, I. Baudin, M.-L. Janex, Understanding membrane fouling: A review over a decade of research, Water Sci. Technol.: Water Supply, 3, (2002), 155-164.
[20] L.D. Nghiem, S. Hawkes, Effects of membrane fouling on the nanofiltration of pharmaceutically active compounds (Phacs): Mechanisms and role of membrane pore size, Sep. Purif. Technol., 57, (2007), 176-184.
[21] A.I. Schäfer, L.D. Nghiem, N. Oschmann, Bisphenol A retention in the direct ultrafiltration of greywater, J. Membr. Sci., 283 (2006) 233-243.
[22] L.D. Nghiem, D. Vogel, S. Khan, Characterising humic acid fouling of nanofiltration membranes using bisphenol A as a molecular indicator, Water Res., 42 (2008), 4049-4058).
[23] H.R. Buser, T. Poiger, M.D. Muller, Occurence and environmental behavior of the chiral pharmaceutical drug ibuprofen in surface water and in wastewater, Environ. Sci. Technol., 33 (1999) 2529-2535.
[24] J. Hollender, Micropollutants - Occurrence in Swiss surface waters and assessment, GWA, 11 (2007) 843-854.
[25] Stadt Zürich Wasserversorung, Jahresbericht 2007 Seewasser Lengg, www.stadt-zuerich.ch/internet/wvz/home/wasserqualitaet/verteilsys.ParagraphContainerList.ParagraphAdditionalInfo.ParagraphList.0002.File.pdf/lengg.pdf
[26] K.M. Lewis, R. D. Archer, P_{ka} values of estrone, 17[Beta]-estradiol and 2-methoxyestrone, Steroids, 34 (1979) 485-499.
[27] A. Avdeef, K.J. Box, J. E.A. Comer, C. Hibbert, K.Y. Tam, Ph-metric Logp 10. Determination of liposomal membrane-water partition coefficients of ionizable drugs, Pharm. Res., 15 (1998) 209-215.
[28] J. Pieracci, J. V. Crivello, G. Belfort, Photochemical modification of 10 KDa polyethersulfone ultrafiltration membranes for reduction of biofouling, J. Membr. Sci., 156 (1999) 223-240.
[29] P.A. Neale, B.I. Escher, A.I. Schäfer, Quantification of solute-solute interactions using negligible - depletion solid phase microextraction: Measuring the affinity of estradiol to bulk organic matter, Environ. Sci. Technol., 42 8 (2008) 2886-2892.

[30] Mulder, M. Basic principles of membrane technology, Kluwers Academic Publisher, Dordrech, 2000.
[31] M. Carballa, G. Fink, F. Omil, J.M. Lema, T. Ternes, Determination of the solid-water distribution coefficient (Kd) for pharmaceuticals, estrogens and musk fragrances in digested sludge, Water Res., 42 1-2 (2008) 287-295.
[32] H. Yamamoto, H.M. Liljestrand, Y. Shimizu, M. Morita, Effects of physical-chemical characteristics on the sorption of selected endocrine disrupters by dissolved organic matter surrogates, Environ. Sci. Technol., 37 (2003) 2646-2657.
[33] D. Jermann, W. Pronk, S. Meylan, M. Boller, Interplay of different NOM fouling mechanisms during ultrafiltration for drinking water production, Water Res., 41 (2007) 1713-1722.
[34] Y. Yoon, P. Westerhoff, J. Yoon, S.A. Snyder, Removal of 17 Beta Estradiol and Fluoranthene by nanofiltration and ultrafiltration, J. Environ. Eng.-ASCE, 130 (2004) 1460-1467.
[35] L.D. Nghiem, Removal of emerging trace organic contaminants by nanofiltration and reverse osmosis, The University of Wollongong, Australia, 2005.
[36] L.D. Nghiem, J. Mc Cutcheron, A.I. Schäfer, M. Elimelech, The role of endocrine disrupters in water recycling: Risk or mania, Water Sci. Technol., 50 (2004) 215-220.
[37] W. Yuan, A.L. Zydney, Humic Acid Fouling During Microfiltration, J. Membr. Sci., 157 (1999) 1-12.
[38] A.R. Costa, M.N. de Pinho, M. Elimelech, Mechanisms of colloidal natural organic matter fouling in ultrafiltration, J. Membr. Sci., 281 (2006) 716-725.
[39] E. M. V. Hoek, M. Elimelech, Cake-enhanced concentration polarization: A new fouling mechanism for salt rejecting membranes, Environ. Sci. Technol., 37 (2003) 5581-5588.
[40] T.H. Chong, F. . Wong, A.G. Fane, Enhanced concentration polarization by unstirred fouling layers in reverse osmosis: Detection by sodium chloride tracer response technique, J. Membr. Sci., 287 (2007), 198-210.
[41] C.W. Carter, I. H. Suffet, Binding of DDT to dissolved humic materials, Environ. Sci. Technol., 16 (1982), 735-740.
[42] A.E. Childress, M. Elimelech, Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes, J. Membr. Sci., 119 (1996) 253-268.
[43] W. Stumm, J. Morgan, Aquatic Chemistry, John Wiley and Sons Inc., New York 1995.

Jerman, D. ; Pronk, W. ; Boller, M. ; Schäfer, A.I. ; (2009) The role of NOM fouling on the retention of estradiol and ibuprofen during UF for drinking water production, Journal of Membrane Science, 329, 75-84.

Table 1 Physiochemical properties of estradiol (25) and ibuprofen (26) and their molecular structures.

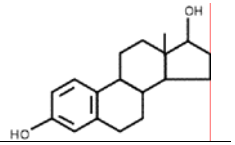
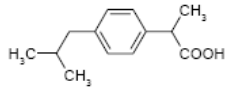
Compound	MW	pKa	Log Kow	Molecular structure
Estradiol	270	10.7	4.0	
Ibuprofen	206	4.1	4.0 (de-ionized)	

Table 2 Log K_{oc} values for estradiol with humic acids and alginate.

Estradiol	Log K_{oc}	Reference
Aldrich HA	4.21*	(28)
	4.94	(31)
IHSS HA	4.92	(31)
Alginate	3.96*	(28)
	3.75	(31)

Table 3 Observed retention of estradiol and ibuprofen and impact of NOM on the retention of estradiol and ibuprofen during UF using a hydrophobic (Biomax) and a hydrophilic (RC) membrane. Arrows up indicate an increase, arrows down a decrease, horizontal arrows indicate no influence.

	Retention of micropollutant during UF and impact of UF fouling by NOM							
Micropollutant	**Estradiol**				**Ibuprofen**			
Membrane	**Hydrophobic**		**Hydrophilic**		**Hydrophobic**		**Hydrophilic**	
No NOM	*Retention*	*Retention mechanism*	*Retention*	*Retention mechanism*	*Retention*	*Retention mechanism*	*Retention*	*Retention mechanism*
	Very large (≈780 mg/m²)	Large hydrophobic adsorption of estradiol onto the membrane	Low	Few adsorption of estradiol onto the membrane	Low	Few hydrophobic adsorption of ibuprofen onto the membrane	Insignifi-cant	Rejection between negatively charged ibuprofen and membrane
With NOM	*Impact of NOM*	*Mechanism of impact*	*Impact of NOM*	*Mechanism of impact*	*Impact of NOM*	*Mechanism of impact*	*Impact of NOM*	*Mechanism of impact*
Aquatic humic acid MW < MWCO	→	**HA membrane adsorption:** lowers charge and hydro-phobicity of membrane	→		→	**HA membrane adsorption:** lowers charge and hydro-phobicity of membrane	→	
Aldrich humic acid MW ≈ MWCO	↗	**Cake formation:** increases re-tention by estradiol par-titioned onto HA and by effect of fouling layer.	↗	**Cake formation:** increases re-tention by estradiol par-titioned onto HA and by effect of fouling layer.	→	**Cake forma-tion and/or HA membrane adsorption:** both can decrease retention (see above or below)	→	
Alginate MW ≈ MWCO	↗	**Cake/gel formation:** increases re-tention mainly by effect of fouling layer and by estradi-ol partitioned onto alginate.	↗	**Cake/gel formation:** increases re-tention mainly by effect of fouling layer and by estradi-ol partitioned onto alginate.	→	**Cake/gel formation:** decreases re-tention by cake-enhanced concentration polarization.	→	**Cake/gel formation:** decreases re-tention by cake-enhanced concentration polarization.

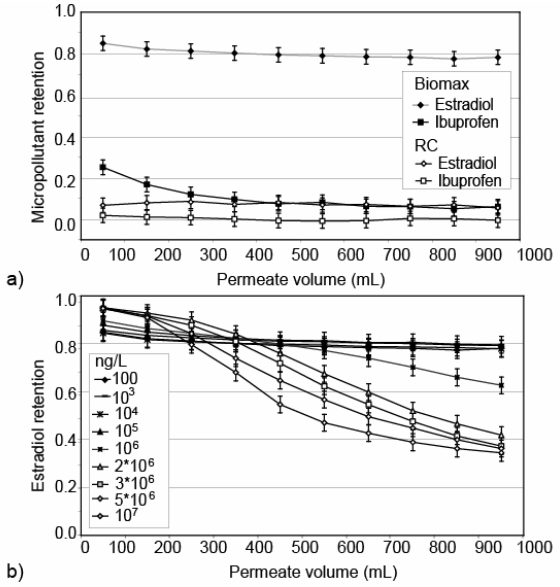


Figure 1 UF of estradiol and ibuprofen: a) Retention by hydrophobic (Biomax) and hydrophilic (RC) membrane, b) Retention of estradiol by hydrophobic (Biomax) membrane for solutions with different estradiol concentrations.

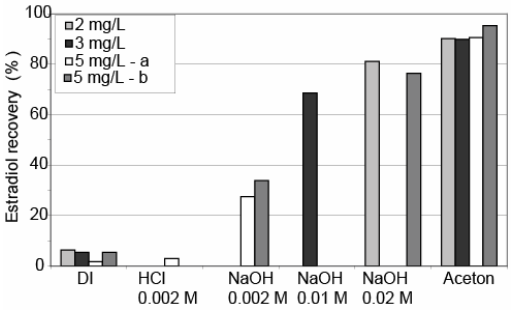


Figure 2 Estradiol recovered from the membrane by deionized water (DI), HCl, NaOH and acetone after filtration of solutions with 2, 3 and 5 mg estradiol/L. 100% refers to the estradiol retained on the membrane on the basis of an estradiol UF mass balance of 1 L solution. Experiments performed in duplicate are differentiated by a and b.

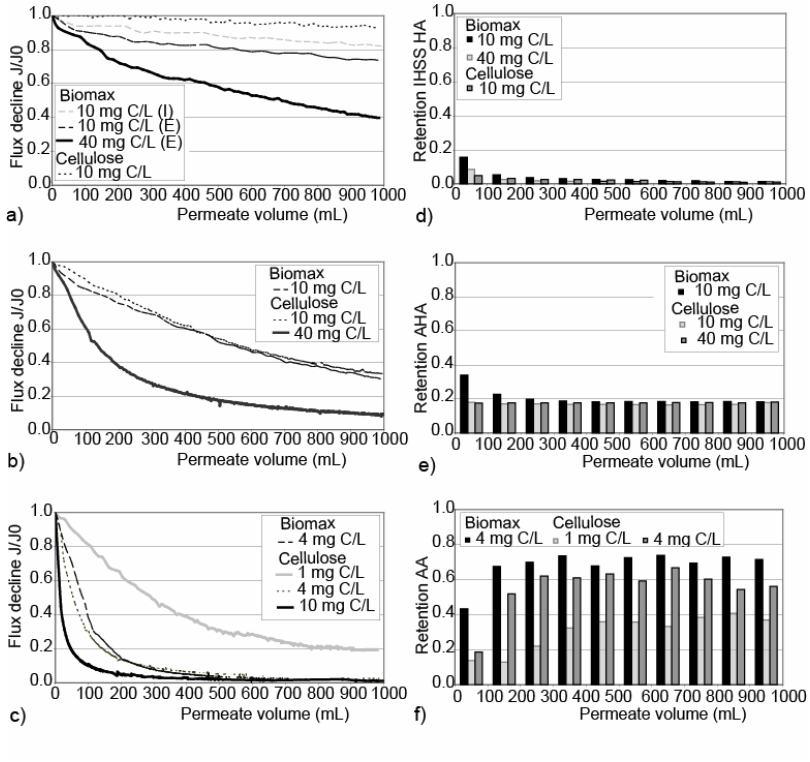


Figure 3 Flux declines and NOM retention during UF of NOM with estradiol and ibuprofen using the hydrophilic (cellulose) and hydrophobic (Biomax) membrane a) and c) IHSS humic acid (IHSS HA) b) and e) Aldrich HA (AHA), c) and f) alginate (AA). In Figure 3a, the flux reductions for NOM solution with estradiol (E) or ibuprofen (I) are given separately due to significant differences not observed in Figures 3b and 3c.

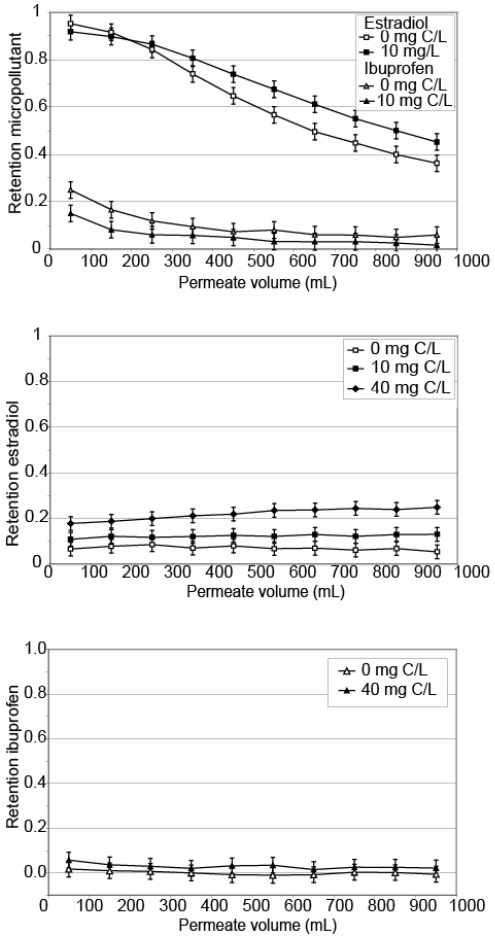


Figure 4 Estradiol and ibuprofen retention in the presence of Aldrich humic acid (given in mg C/L) a) estradiol and ibuprofen using the hydrophobic (Biomax) membrane, b) estradiol using the

hydrophilic (RC) membrane at different concentrations of Aldrich HA, c) ibuprofen using the hydrophilic (RC) membrane.

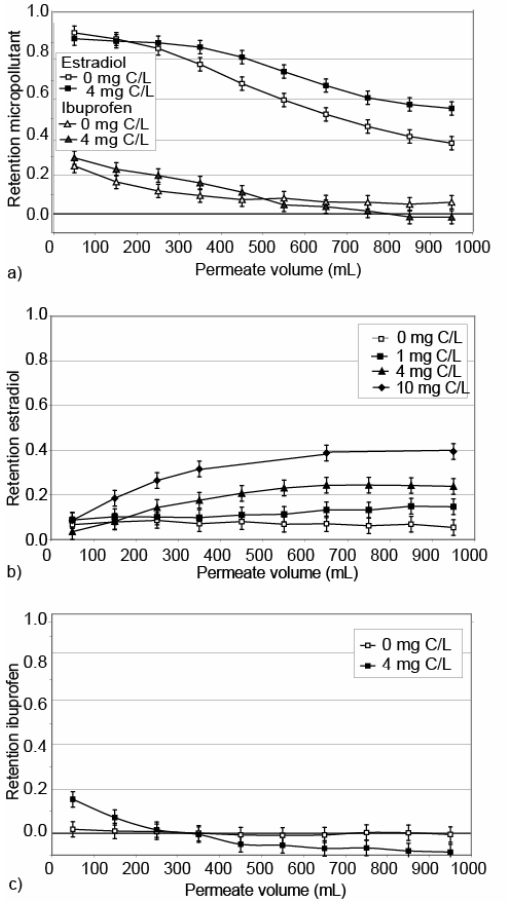


Figure 5 Estradiol and ibuprofen retention with different concentrations of alginate (given in mg C/L) a) estradiol and ibuprofen with the hydrophobic (Biomax) membrane, b) estradiol with the hydrophilic (RC) membrane at different concentrations of alginate, c) ibuprofen with the hydrophilic (RC) membrane.

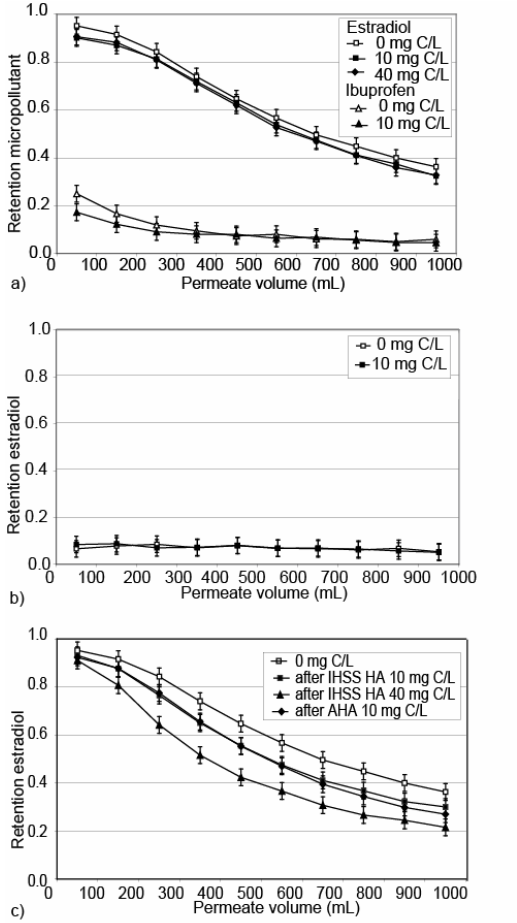


Figure 6 Retention with different concentrations of IHSS HA (given in mg C/L) a) Estradiol and ibuprofen retention by the hydrophobic (Biomax) membrane, b) estradiol retention by the hydrophilic (RC) membrane, c) estradiol retention by the hydrophobic (Biomax) membrane pre-fouled with IHSS and Aldrich HA (AHA).

SUPPORTING INFORMATION

Two additional experiments were performed to confirm the occurrence of concentration polarization during the batch ultrafiltration experiments performed in our study. The hydrophilic (RC) membrane was used, the solution in the stirring cell being unstirred (blank) in the first experiment and stirred (100 rpm) in the second one. The results are shown in Figure S1a. It can be seen that the retention of ibuprofen was initially positive and then decreased to negative values when the solution remained unstirred. In contrast, the retention of ibuprofen was negligible except for a slight increase during the first 200 mL of filtration when the filtration was stirred. As stirring strongly reduces the concentration polarization at the membrane surface (1), this indicates that such polarization was present in the experiments with an unstirred solution. Moreover, it can be seen in Figure S1b that stirring reduced the flux decline indicating reduced fouling. This correlates with a reduced/negligible concentration polarization of ibuprofen when the solution was stirred compared to when it was unstirred.

Figure S1 Stirred and unstirred ultrafiltration of alginate 4 mg C/L and ibuprofen a) ibuprofen retention, b) relative flux decline.

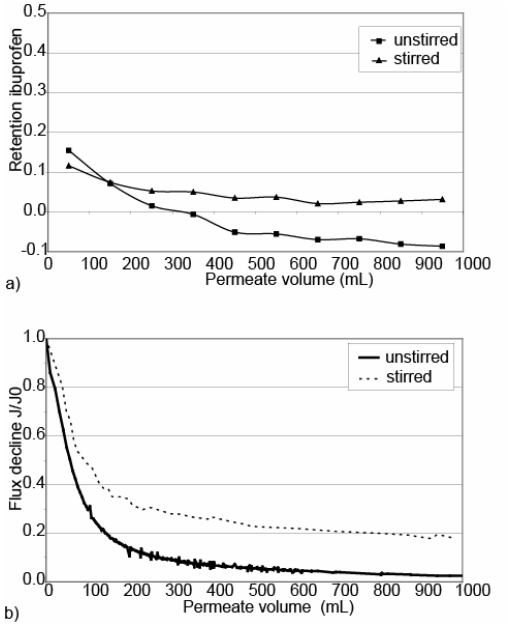


Figure S1 Stirred and unstirred ultrafiltration of alginate 4 mg C/L and ibuprofen a) ibuprofen retention, b) relative flux decline.

REFERENCES

[1] M. Mulder, Basic principles of membrane technology, second edition, Kluwer Academic Publisher, Dordrecht, 2000.